

**A STUDY OF ENAMEL FILM STRENGTH
AS AFFECTED BY THE PROPERTIES
OF THE ENAMEL BEFORE, DURING,
AND AFTER DRYING**

BY
MELBOURNE KENNETH BLANCHARD
B.S., University of Illinois, 1938
M.S., University of Washington, 1939

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
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I. INTRODUCTION

A. *Purpose of the Study*

Since film strength and tearing have long been subjects of controversy, the following investigation was undertaken to add to the reliable information on the subject.

B. *Survey of Literature*

Several authors have reported on studies of the tearing tendency of enamels as related to the soluble salts in the mill liquor. These investigators¹⁻⁷ have found that the principal salts dissolved from enamel frit are borax, various sodium borates, and sodium sulfate. From the results of their studies, several theories of tearing have been advanced. Rosenberg and Langerman⁵ attributed tearing to shrinkage of borax during melting, and claim that the function of sodium nitrite is to mechanically bond the enamel at a low temperature, holding it together until fusion. Lange⁷ agrees with Rosenberg and Langerman as to the mechanism of sodium nitrite in preventing tearing. Hurst and Andrews⁶ show data indicating that tearing is due to the expansion occurring when boric acid and boric oxide compounds are dehydrated, causing rupture in the enamel film. Combined with this is the effect of molten boric acid in drawing the separate patches of torn enamel together to form balls. The mechanism by which NaNO_2 is effective in reducing tearing, appeared to be the result of the formation of sodium metaborate upon reaction with boric acid. Sodium metaborate was found to have a low dehydration expansion, and little effect in the fused state, thus eliminating the causes of tearing.

II. PROCEDURES AND RESULTS

A. *Visual Observations of Tearing During Firing*

The progress of tearing was observed during the heating

of various enamel samples in a small furnace which was equipped with a quartz window. The six different enamels studied were standard white cover coats characteristic of the different types used commercially. To promote tearing, 0.2 percent of boric acid, based on 100 parts of frit, was added.

The progress of tearing was observed to be the same for all enamels studied, and may be outlined as follows:

- (1) The formation of hair line mud-cracks in the enamel surface at very low heat.
- (2) A widening of the cracks caused by shrinkage in the enamel, accompanied by a lifting of the layers at the crack edges, away from the ground coat.
- (3) A flattening of the separate patches, accompanied by rounding of the crack edges, and fusion with the ground coat.
- (4) Melting together of the cracks, each crack being filled with the blue ground coat which was carried up between the cracks during fusion.

B. *Observations of Drying Behavior of Enamel Films*

Observations of enamel samples showed that the cracks with which tearing began were present after the drying. The drying stresses causing these cracks were studied by drying enamel films on non-rigid bases and noting the bending of the coated bases after drying. Tearing and non-tearing enamel slips were applied on strips of thin celluloid, tin-foil, waxed paper, and very thin shim stock. In all cases the drying stresses in each type of enamel were the same. The tearing enamels bent during drying so that the originally level, non-rigid base assumed a U curvature in which the ends of the sample were higher than the middle. The non-tearing enamels remained flat throughout the drying. The total drying shrinkages were the same for both types of enamels (approximately 35%) but the strain occurring in the tearing enamel appeared to be the result of surface shrinkage being completed before internal drying had progressed to the same degree.

C. *Study of Textural Properties of Enamel Films*

Since there are differences in the surface characters and

shrinkage behaviors of dried enamel films, a study was made of the textural characteristics and their relation to film strength and resistance to the forces of shrinkage. Thin sections were cut parallel and perpendicular to surfaces of a number of tearing and non-tearing enamels, and a microscopic study of the sections was made. Observations of these sections showed that the tearing enamels were all more densely packed than the non-tearing enamels with which they were compared. The tearing enamels had very fine networks of pores while the non-tearing enamels were loosely packed, with large pore spaces. In the case of the tearing enamels, the density of packing shows why the drying behavior is as it was observed. The capacity for denser packing and the finer pore structure hinders drying so that the moisture gradient is effective in setting up the tearing stresses. Careful measurements of water loss vs. time for tearing and non-tearing enamels substantiate this last as the non-tearing enamel was found to reach dryness more quickly than the tearing enamel. The non-tearing enamels, on the other hand, have the open structure essential to even drying and even shrinkage. In addition, the good enamels are capable of absorbing any shrinkage stress, even or uneven, because of their networks of large open pores. In effect, the film strength of the non-tearing enamel appears to be actually "film weakness," in that the cracking that would free the stress in a dense enamel occurs as a single tear, while the same stress could be absorbed by hundreds of cracks in the loosely packed enamel.

D. Consideration of Chemical and Physico-Chemical Effects Responsible for Packing Characteristics of Tearing and Non-Tearing Enamels

The only variables allowed to enter into the determination of the characteristics of the tearing and non-tearing enamels studied were the soluble salts and their concentrations. In relating the packing densities of dried enamels to their soluble salt contents, the principal effects were due to the amount of Na^+ ions furnished by the dissolved sodium salts in the slip.

The effect of Na^+ ions on an enamel-like slip is shown in Curve 1 of Figure 1. This curve represents the change in

pick-up or viscosity of a clay-water-quartz-electrolyte slip to which has been added increasing quantities of NaOH. Curve 2 of Figure 1 represents the change in pick-up of the same type of slip with increasing additions of a concentrated mill-liquor from a non-tearing enamel. The slip to which the mill liquor was added shows the same characteristics as the slip containing NaOH, but not to as marked a degree. The mill liquor slip, as indicated in Figure 1, has a good "set" in the trough region of the curve; while the NaOH slip is very thin in the same region.

The property of "set" or slip viscosity, as fixed by the ions present and the ion adsorption characteristics of the clay fraction of the system, have been related directly to the tearing tendency. The regions of tearing, and of non-tearing slips are shown on the curves of Figure 1; the tearing being most severe in the trough region of the NaOH slip. The slips with the proper set are non-tearing slips. The physical difference in the tearing and non-tearing slips is in the state of aggregation of the particles in the systems. The slip that is "set up" by the proper concentration of Na^+ ions is said to be coagulated, and is made up of clusters of particles, grouped loosely and having between them large pore spaces. The thin, or dispersed slip is one in which the particles remain separated from each other, and are free to pack during drying with small pore spaces.

The drying behaviors of the two types of slips are governed by the nature of the particle aggregation. A coagulated slip dries uniformly, and any shrinkage strain may be absorbed in the large pores of the system. The fine pore size of the dispersed slip hinders drying so that a moisture gradient exists, and a drying strain results.

E. Consideration of the Effects of Specific Electrolytes on the Tearing Tendency

Boric acid has long been known to be effective in producing tearing when added to an enamel slip in small quantities. The dotted lines of Figure 1 show the effect of a 0.04% boric acid addition on consistency and tearing resistance of the NaOH and mill liquor slips. The viscosities of both slips were

FIGURE 1. EFFECT OF NaOH AND MILL LIQUOR ADDITIONS ON CONSISTENCY OF SLURIES OF FINE-TEXTURED CLAY (a) WHITE; (b) RED.

reduced in their regions of best set, and tearing occurred as indicated. The action of boric acid appears to be one in which a chemical reaction produces a new salt that fixes the Na^+ ion concentration at a constant level over the range studied. This level of Na^+ ion concentration is such that the slip is relatively dispersed, and will tear during drying.

The buffer salt in the case of the boric acid additions to slips containing Na^+ ions, as in the case of an enamel slip, appears to be borax. The quantity of borax that could be formed in reaction of NaOH with the quantity of H_3BO_3 added to the slips of Figure 1, was approximately 0.6 grams. This amount of borax was added to a slip containing no other electrolyte, and as shown in Figure 1, the viscosity of the slip was reduced to the constant level noted for the other two slips.

To prevent or correct the tearing tendency brought about by the insufficient quantity of sodium ions furnished by a buffer such as borax, the action of the buffer can be properly changed by the addition of an ionizable sodium salt. Those found⁶ to be effective are: NaNO_2 , Na_2CO_3 , NaBO_2 and NaCN . Other sodium salts are also effective, but are undesirable because of the blistered enamels resulting from decomposition during firing, of the salt anions.

F. *Considerations of the Effect of Firing on Enamel Films*

The shrinkage of early firing seems to have only the effect of enhancing any film defect that exists after drying is complete. Hurst and Andrews⁶ have discussed the viscosities of the various salts during fusion, and they report the effects to be such that the tearing tendency is enhanced by heating, the separate patches of torn enamel being drawn away from the previously formed ruptures.

III. CONCLUSIONS

Observations of the results of this study offer the following conclusions:

1. Enamel tearing is a defect resulting from the shrinkage stresses set up in an enamel film during drying and very early firing combined with the inability of the film to prop-

erly absorb these stresses.

2. The capacity of a non-tearing enamel to resist tearing is due to the absence of a strain gradient during drying coupled with a loose, weak, texture.
3. The characteristic shrinkage and resultant strain gradient in a tearing enamel is due to the packing character of the enamel during drying.
4. The packing character of an enamel is determined primarily by the state of aggregation of the enamel slip as determined by the kind and quantity of adsorbed ions present. The ion most effective in enamel slips is the Na^+ ion freed upon solution of frit glass. The final state of aggregation of a dry enamel is influenced in extreme cases by the total quantity, disposition, and crystalline characteristics of the soluble salts present.
5. Boric acid, when added to an enamel slip, causes tearing by forming a buffer salt (borax probably) that disperses the slip, allowing it to pack so that strain and tearing result. Sodium nitrite and a number of other salts prevent tearing by properly repressing the buffer and balancing the Na^+ ion concentration to give the enamel the proper characteristics.

FOOTNOTES

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VITA

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